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Steam treatment of four softwood species and bark to produce torrefied wood

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HIGHLIGHTS

- Steam treatment is introduced as a wet torrefaction process at lower temperatures.
- The heating value of steam treated biomass is comparable to that of dry torrefaction.
- The increased carbon content also confirms the effectiveness of the pretreatment.
- Among different softwood species, Spruce is affected by steam treatment the most.
- Bark particles is affected by steam treatment the least..

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ABSTRACT

Debarked samples from three wood species (Spruce, Douglas-fir and Pine) and Douglas-fir bark were treated with saturated steam at 220 °C for 5 min. The objective was to quantify physical and compositional properties of the treated biomass that would affect on the degree of carbonization (torrefaction) of softwood particles. The resulting data indicated that the calorific value increases as a result of steam treatment; the highest increase was 26.0% for Spruce, from 18.7 MJ/kg to 23.6 MJ/kg. The corresponding carbon content of the treated Spruce increased from 46.5% to 57.0%. The equilibrium moisture content of the treated wood, placed in a chamber at 90% relative humidity and 30 °C air for 180 min, dropped from around 0.103 (decimal dry basis) (before treatment) to about 0.045 (decimal dry basis) for Spruce treated particles. Bulk density of Spruce particles increased the most from 87 kg/m^3 to 129 kg/m^3 after steam treatment. The bulk density of Douglas-fir bark decreased from 310 kg/m^3 to 275 kg/m^3 upon steam treatment. The increased values in calorific values, hydrophobicity, carbon content and dark brownish color indicated a mild degree of torrefaction of biomass when compared to the corresponding values of treated biomass at temperatures of 280 °C.

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1. Introduction

Raw cellulosic feedstock is bulky and has high moisture content. These two undesirable characteristics alone make raw biomass costly to store, transport, and difficult to feed into a thermal reactor. A dense and flowable pelletized feedstock with low and uniform moisture content outperforms loose feedstock [1]. Wood pellet production and export have experienced rapid growth in recent years. In 2010, Canada's 37 pellet plants operated at about 65% their capacity, producing about 1.3 million metric ton (t) per year. The pellet production increased in 2011 when almost 1.9 million t of pellets were exported to Europe, USA and Japan for heat and power generation [2].

The growth of wood pellet industry in the context of international trade is hampered by two major properties, physical stability and density. A low durable pellet tends to break and to generate dust during its frequent handlings and storage. Similarly the cost of transporting the low density pellets is more than the highly dense pellets. Initially, wood pellets were made from compacting clean saw dust residue available from saw mills. Recently, the availability of sawmill residues have lessened due to a slowdown in the housing market and increased number and production capacity of wood pellet plants. An increasing number of pellet producers are using a greater proportion of forest wastes like logging residues and bark as feedstock. Unfortunately the non-homogeneity of the feedstock results in low mechanical stability of pellets. In addition to a low mechanical strength, the issue with a low energy density wood pellet as compared to coal is a serious one for an exporting country like Canada where wood pellets travel

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long distances and often over oceans. Improving the mechanical strength and energy density of wood pellets would also help a larger proportion of biomass to be co-fed with coal to produce heat and electricity. Therefore improving energy density and strength of pellets are two key factors for a continued growth of the industry.

Torrefaction is a pyrolytic process that subjects a feedstock to thermal treatment at relatively low temperatures of 250–300 °C in a reduced or absence of oxygen environment. Torrefaction can convert diverse lignocellulosic biomass feedstocks into an energy-dense and homogeneous solid biofuel [3]. The main principle of torrefaction from a chemical point of view is the removal of elemental oxygen to lower O/C ratio compared to the original biomass [4]. Torrefied biomass is compacted to produce the second generation biomass pellets to address the problems of low heating value per unit volume. Torrefied pellets exhibit a number of other desirable properties like hydrophobicity and low off-gas emissions, when compared to the current regular pellets [5–9]. The downside of torrefaction is its detrimental effect on natural binding capacity of the treated biomass to form pellets.

Gilbert et al. [8] and Stelte et al. [9] confirmed that pellets produced from torrefied biomass were not as durable as untreated pellets. It was also shown that torrefaction increased friction in the channels of the press mill resulting in generation of excessive heat and burning of biomass. Pellets from torrefied wood were more brittle and less strong compared to untreated pellets. Therefore, it is important to explore ways of torrefying and densifying wood to achieve mechanically strong and stable torrefied pellets.

Different inert media but mostly nitrogen have been used for biomass torrefaction. Yan et al. [10] torrefied ground Loblolly Pine in hot compressed water (water to biomass ratio of 5:1 on weight basis) at 200–260 °C and pressure up to 4.8 MPa (700 psi). The study showed that wet torrefaction increased carbon content of the biomass from 50% to 72% and decreased oxygen content from 43% to 23%, depending on temperature. The increase in carbon percentage was much higher in wet torrefaction at 260 °C for 15–30 min residence time, compared to dry torrefaction (with nitrogen) at 300 °C after 80 min. Yan et al. [10] did not report data on bulk density and flowability of treated material.

Saturated steam pretreatment has increased the binding quality of woody material [11–13]. Lam et al. [11] showed that pellets made from ground debarked Douglas-fir (D. Fir), steam treated with saturated steam at 200–220 °C for 5 or 10 min, were harder and more dimensionally stable than pellets made from untreated wood. The calorific value of the ground particles increased from 18.82 MJ/kg for untreated to 20.09 MJ/kg for wood treated at 220 °C for 10 min.

Knowing the positive effect of steam treatment on the binding characteristics of D. Fir particles, the objective of this research is to extend these studies to three species of softwood Pine, Spruce, and D. Fir bark. Debarked ground D. Fir was also included in these tests. The objective was to understand whether steam treatment of ground wood particles has differing effects on compositional and functional characteristics of ground particles. The four samples were treated with saturated steam at 220 °C for 5 min following Lam et al. [11]'s conclusion that this temperature–time combination produced the hardest pellets. Properties of treated and untreated materials were measured and compared with properties found in published literature for dry torrefied material. The compositional and functional properties of pellets made from these treated wood species will be presented in a companion paper.

2. Materials and methods

2.1. Materials

The biomass tested in this research consisted of three white softwood species, Pine (*Pinus contorta*), Spruce (*Picea glauca*), and Douglas-fir (D. Fir) (*Pseudotsuga menziesii*), and one sample of bark extracted from D. Fir. Pine, Spruce, and D. Fir constitute major species of forests in British Columbia (BC), Canada. Large pieces of Pine and Spruce lumber were provided by the Centre for Advanced Wood Processing, Faculty of Forestry, the University of British Columbia. The samples came originally from Williams Lake forests in central BC. Samples of D. Fir white wood and bark were provided by Malcolm Knapp Research Forest, located in Maple Ridge, BC (near Vancouver). The freshly cut stem wood pieces were brought to the lab and debarked manually. The prepared samples were spread on a stack of wire mesh trays in the lab to be dried from about 50% moisture content (w.b.) to about 20% (w.b.). Moisture contents were determined using the convection drying oven method according to the ASAE standard S358.2 [14].

2.2. Sample preparation

The dried large stems of each sample were cut using a band saw (Craftsman 14" band saw, Sears Canada Inc.) to smaller pieces (approximately 40 × 40 × 80 mm). The pieces were then ground in a hammer mill (Model 10HMBL, Glen Mills Inc., Clifton, NJ) with the screen size of 1.6 mm. The moisture content (m.c.) of ground samples was further adjusted to 10% (w.b.) either by drying the moist material at 20% m.c. (w.b.) in a convection oven at 50 °C or by spraying distilled water on the sample if the m.c. was found to be less. About 500 g material (for each species) was conditioned, and subsequently divided into batches (25 g each batch) for steam treatment.

2.3. Steam treatment

Steam treatments were carried out in a 1 L high-pressure vessel. The treatment setup was previously developed and calibrated at the Clean Energy Research Centre Laboratory, University of British Columbia [11]. Approximately 25 g of each sample of ground conditioned wood was fed to the preheated reactor while its wall temperature was maintained at 220 °C. Saturated steam at 220 °C was fed to the treatment vessel for 5 min. The treated sample was discharged at once through a gate valve into a plastic bag placed in a collection container. Plastic bag with its contents was transferred to cool storage for further analysis. Prior to storage, the moisture content of the solids was measured in triplicates.

2.4. Physical and compositional property measurements

The following paragraphs describe briefly methods used to determine physical and compositional characteristics of the treated and untreated samples.

The size distribution of both treated and untreated ground samples was determined according to the ASAE standard S319.4 [15]. Prior to sieving analysis, wood samples were conditioned to 10% m.c. (w.b.). Approximately 20 g of each species was placed on top of a stack of sieves. The sieve series selected were based on the range of particles in the sample [16]. For the grounds from 1.6 mm hammer mill screen opening, sieve numbers were 20, 30, 40, 50, 70, 100, 140, 200 corresponding to nominal US sieve openings 0.841, 0.595, 0.420, 0.297, 0.210, 0.149, 0.105, and 0.074 mm, respectively [15]. The set of sieves plus a pan were placed on a Ro-Tap sieve shaker (Tyler Industrial Products, OH USA). The duration of sieving was 10 min, which was previously determined through trials to be optimal [16]. The material retained on each sieve was weighed on an electronic balance to 0.01 g precision. The geometric mean diameter (d_{gm}) and geometric standard deviation (S_{gm}) of particle diameter were calculated according to ANSI/ASAE S319.4 [15]. The sieving test was repeated three times for each sample.

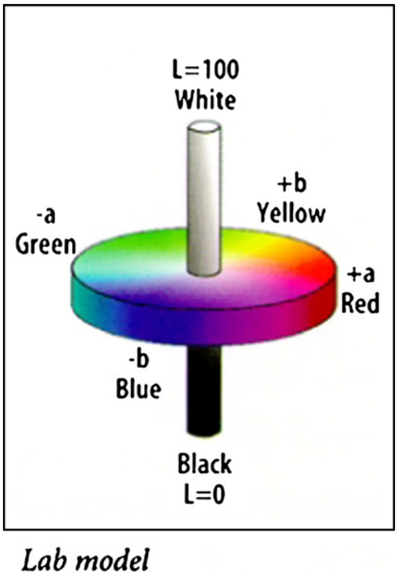

Fig. 1. *L*, *a*, *b* components of color in the *Lab* system.

The ash content of each sample was measured in triplicate using NREL method [17]. The higher heating value (HHV) of solid samples was determined in an oxygen bomb calorimeter (Model 6600, Moline, IL) fitted with continuous temperature recording. A small mass 0.6–1.2 g of ground sample was densified manually in the Parr pelleter and placed in the instrument chamber. The measurements were repeated three times (three different pellets). The carbon, hydrogen, nitrogen and sulfur contents of wood samples and bark were determined on dry basis using a CHNS analyzer (Model 2400 series II, PerkinElmer Company, MA USA). Assuming that only oxygen can be found in the woody material aside from these elements, we calculated the oxygen content by subtracting the sum of these measured components from 100%. These measurements were repeated twice for each untreated and treated material.

The color of each sample was measured in triplicate using Spectrophotometer CM-5 (Konica-Minolta). The color was characterized using a three-dimensional ($L\ a\ b$) color scale as shown in Fig. 1. The scale L ranges from 0 for black to +100 for white; the scale a ranges from −50 for green[1] to +50 for red; and the scale b ranges from −50 for blue to +50 for yellow. The color coordinate values for each sample before and after steam treatment were measured. A differential color composite ΔE was calculated as an indicator of color deviation between treated and untreated samples,

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \tag{1}$$

where subscripts 1 and 2 represent sample 1 (untreated) and sample 2 (treated).

Bulk density was calculated following the method previously used by Mani et al. [16] for ground cellulosic material. A glass cylinder with a volume of 25 mL and inside diameter of 25.4 mm (about 50 times larger than the maximum of average particle sizes among the samples) was used. A funnel was filled with the biomass powder. The biomass powder was poured freely into the cylinder from a height of 200 mm. Overflow excess material was stroke off gently from the top of the cylinder by a rubber-coated steel rod [16]. The ratio of mass of the sample divided by the occupying volume of sample in the glass cylinder was calculated as the bulk density (loose bulk density). For tapped density, the loosely filled glass cylinder was tapped on the laboratory bench 15 times, while any produced free volume on top was again filled up with the material [18]. Bulk and tapped densities were determined in triplicates for each sample. The particle solid density was determined using a Quantachrome Multipycnometer (Quantachrome, Boyton Beach, FL, USA). The analysis was done by measuring the pressure difference when a known quantity of pressurized nitrogen flows from a reference volume into the sample cell. The volume of solid particles in the sample cell then is calculated based on the following equation.

$$V_p = V_c - V_R\left[\frac{P_1}{P_2} - 1\right] \tag{2}$$

where V_p is the true volume of biomass grinds (m^3), V_c is the volume of sample cell (m^3), V_R is the reference volume (m^3), P_1 is the pressure reading after pressurizing the reference volume (Pa) and P_2 is the pressure reading after including V_c (Pa). The density (bulk and particle) was calculated from dividing mass over volume (V_p in case of particle solid density).

Inter particle porosity (ε_o) provides packing information of the biomass grinds inside a known container and is determined by the following equation:

$$\varepsilon_o = 1 - \frac{\rho_b}{\rho_p} \tag{3}$$

where ε_o is packing porosity (decimal), ρ_b is bulk density of ground (kg/m^3), ρ_p is particle density of the ground (kg/m^3). Particle density and porosity for each species were measured three times.

Water adsorption rate of particles was measured by placing 2–3 g of each of the completely dried samples in a controlled environment chamber (Model LHU-113, ESPEC Corp., Japan). The chamber temperature was set at 30 °C with a relative humidity (RH) of 90%. The sample remained in the chamber for at least 180 min [11]. The increase in mass of the sample was measured and recorded every 10 min for the first hour and every 30 min afterwards. The weight recording was continued until it reached a constant value. The moisture content calculated from this final mass was considered as the equilibrium moisture content (M_e) of the material. The kinetics of moisture sorption is represented using the ASABE standard formulation for thin-layer drying [19],

$$\frac{(M - M_e)}{(M_i - M_e)} = e^{-kt} \tag{4}$$

M is instantaneous moisture content (decimal, on dry basis), M_e is equilibrium moisture content (decimal, dry basis), and M_i is initial moisture content (decimal, dry basis). Coefficient k is moisture adsorption rate constant (min^{-1}), and t is exposure time (min) [19].

3. Results and discussions

3.1. Moisture content

The initial moisture content of the raw wood species averaged consistently at 11% (d.b.) with standard deviation of 0.1% (Table 5). The moisture content of treated biomass increased, because of the condensation of steam, exiting the reactor along with the treated material, inside the plastic bags. A portion of the treated material adhered to the inside wall of collection bags. This collection procedure was followed for all samples. The treated samples were dried to about 11% m.c. (d.b.) inside the oven set at 50 °C.

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[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

3.2. Color

Fig. 2 shows pictures of treated and untreated samples. Treated samples were dark in color. D. Fir bark seems to be the darkest. Table 3 lists the color coordinate values *L a b* for untreated and treated samples. The value for coordinate *a* (−50 green to +50 red) varied for untreated samples from a minimum of 2.35 for Pine to a maximum of 15.40 for bark. The value for coordinate *b* (−50 blue to +50 yellow) varied for untreated samples from a minimum 17.1 for Pine to a maximum of 26.9 for bark. The white to black scale *L* (0 black to 100 white) did not vary much among untreated whitewood samples, 71.2 for Pine to 72.8 for D. Fir. The *L* value for bark was 47.8 representing a relatively darker color. The treated samples decreased in the *a* and *b* coordinates compared to the values for untreated samples, except for Pine samples. Most decrease was in *L* values, i.e. all samples became darker as is evident in Fig. 2. The overall color change (ΔE) decreased for whitewood, ranging from 40.4 for Pine to 47.4 for Spruce. Bark had a decrease in overall color coordinate of 36.4.

Zhang and Cai [20] explained that the changes of wood color during steam treatment were caused by a series of chemical reactions. Extractives react with the chemical constituents of wood cell wall under high temperature and humid conditions. During steam treatment furfural and some polysaccharides with low molecular weights are created from hemicelluloses degradation. Changes in lignin and extractives chemistry can also contribute to the color changes. Chromophoric groups (carboxylates and phenol) may be produced within the lignin or extractive molecules at high temperatures and humidity. As these components are dark in color (blue green), they lead to the darker color in wood appearance during steam treatment [20]. The decrease in *a* and *b* values can be explained by these chemical composition changes.

3.3. Particle size distribution

Although the same screen size (1.6 mm) was used for grinding, the final mean particle size of material before treatment varied substantially (Fig. 3). The mean particle diameter of untreated Pine at 0.50 mm was the largest. Raw bark particles (D. Fir bark) at around 0.23 mm had the smallest size. Also, the size reduction due to steam treatment differed among various whitewood samples and bark. Fig. 3 shows the mass fraction of three groups of sizes for the particles before and after steam treatment. For the size category >0.5 mm, the mass fractions decreased as a result of steam treatment. For size category between 0.5 mm and 0.1 mm, a slight increase in mass fractions indicated that a portion of particles in size category >0.5 mm of the untreated material comminuted to smaller particles. The mass fractions in the pan for the untreated species were all low except for the bark that was more than 10%. A larger fraction of steam treated species was present in the pan. Lam [21] explained that fine particles burst out from wood particles due to explosion effect, resulting in formation of finer groups of particles. The size reduction due to the steam treatment was the largest for Pine particles from 0.50 mm to 0.37 mm, or roughly 25% in size reduction. The higher size reduction for Pine samples could have been due to the fact that Pine had more of the larger particles in its initial untreated sample. Boussaid et al. [22] found similar results from steam treatment of D. Fir woodchips. We hesitate to conclude that steam treatment reduced the size of bark particles. Bark had initially smaller particle size before steam treatment, so fragmentation of particles was less likely happen for bark. Bark has a soft structure compared to whitewood [23]. The polysaccharide concentration, cellulose (Glucan) and hemicellulose (Xylan and Mannan) contents in D. Fir bark is much lower than in D. Fir whitewood [23]. Steam treatment attacks the hemicellulose and cellulose structure respectively [23]. These components have crystalline structure. The lower concentration of these compounds in bark samples explains their lesser disintegration compared to whitewood.

3.4. Bulk and particle density

Table 1 lists bulk, tapped and particle density of treated and untreated biomass. Bulk and tapped densities of whitewood samples increased after steam treatment. The loose bulk density of the untreated dry whitewood ranged from 87 (for Spruce) to 175 kg/m^3 (for D. Fir). The bulk density of untreated bark was 310 kg/m^3, almost 1.5 times that of white D. Fir. The loose bulk density of steam treated Spruce increased the most to 129 kg/m^3 and that of D. Fir to 209 kg/m^3. The loose bulk density of treated bark decreased from untreated value of 310 kg/m^3 to 275 kg/m^3.

Tapped density represents a dense fill situation. The higher bulk and tapped densities of treated whitewood samples could be related to the higher ratio of fine particles for these samples after steam treatment (Fig. 3). These fine particles fill the voids that would result in increased mass per unit volume. Particle density values for untreated samples ranged from 1387 kg/m^3 to 1407 kg/m^3. Upon steam treatment, the particle density of whitewood decreased to 1072 kg/m^3 (highest decrease for Spruce). The particle density of bark increased slightly from 1400 kg/m^3 to 1455 kg/m^3.

Grous et al. [24] reported an increase in pore volume (5–9 nm pore size) after steam treatment of Hybrid Poplar. Lam [21] also observed an increase in pore volume in steam treated D. Fir and contributed this increase to the loss of volatiles. The strong smell during treatment of Spruce samples could also indicate more volatile loss for Spruce than other species that did not show as much loss in the particle density (mass). For bark, the percentage of fine particles did not increase after steam treatment (Fig. 3). Robinson et al. [23] evaluated the composition of D. Fir wood and bark samples before and after steam treatment. Their results showed a smaller mass loss for blends containing higher ratio of bark to whitewood. For bark samples, the pore size expansion was more effective on increasing the particle density compared to mass loss due to volatile loss. The porosity (ε_o) (Table 1) is an indicator of packing characteristic of the material, and not the internal pore size of samples. Table 1 shows that the packing porosity of whitewood samples decreased after steam treatment whereas that of bark samples increased. The more expanded bark particles created more void space between particulates in a bulk.

3.5. Ash content and calorific value

Table 2 lists the percent dry basis ash content of the biomass before and after treatment. The ash content in the untreated whitewood ranged from 0.07% in Pine to 0.22% in Spruce, and the ash content of the bark was 2.11%. For treated samples, the ash content increased substantially, ranging from 0.28% in D. Fir to 0.94% in Spruce. The ash content of bark almost doubled from 2.11% to 4.13% after treatment. The standard deviation values for ash content of treated and untreated samples were relatively high and increased for treated samples. Lam et al. also reported the increase in the ash content after steam treatment [11]. As these values are relative, they cannot directly show the increase in metal or inorganic content of samples; it could be an indicator of the relative loss of other components in the samples. Lam showed the loss of hemicellulose sugars after steam treatment of D. Fir [21].

Table 2 lists the higher heating value (HHV) for the treated and untreated biomass. Three species Spruce, Pine, and D. Fir had similar HHV of 18.61–18.81 MJ/kg. Untreated bark had a higher HHV at 19.13 MJ/kg. The HHV increased to 21.16 MJ/kg for Pine, and to 23.58 MJ/kg for Spruce. In all cases, the standard deviation

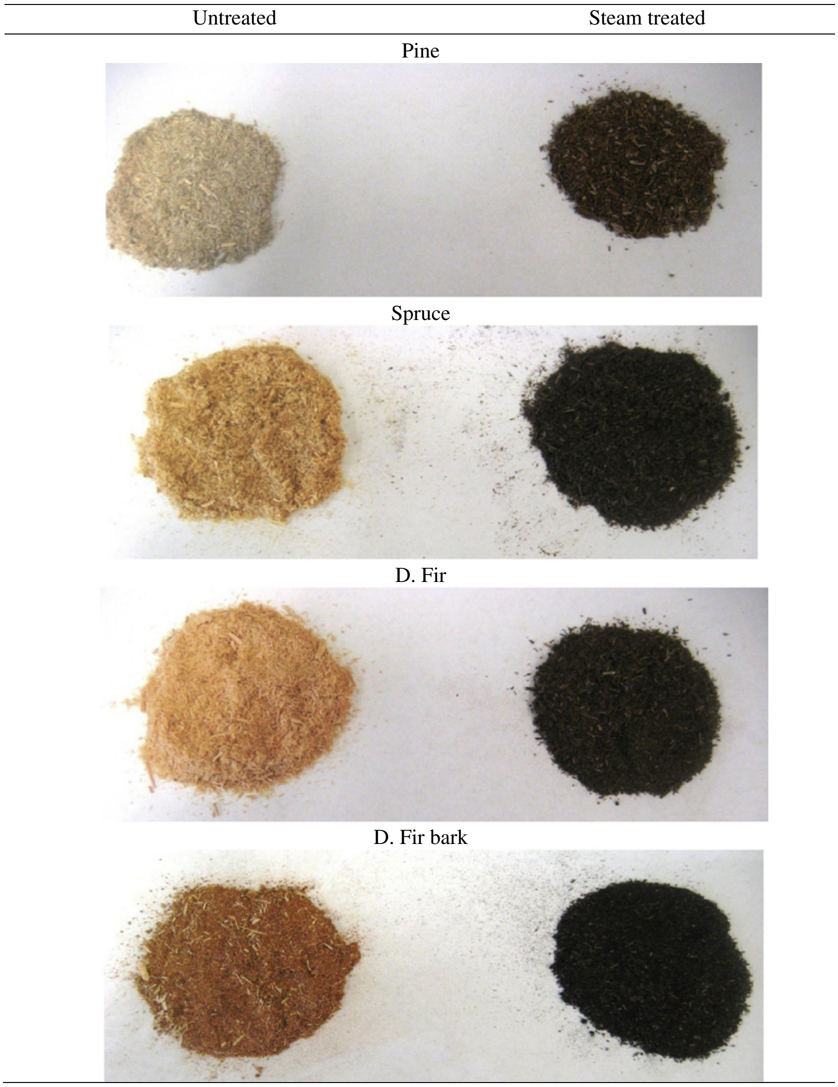

Fig. 2. Photos of untreated (left) and steam treated (right) samples.

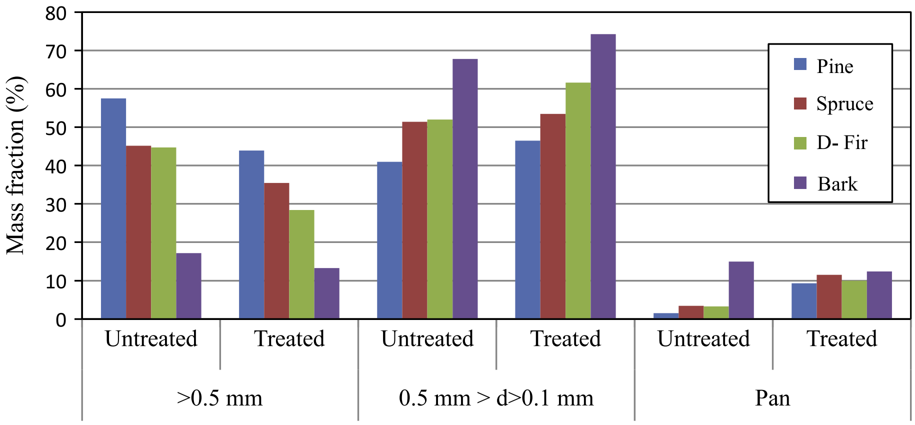

Fig. 3. Size distribution of three size group of particles before and after steam treatment.

values for HHV of each sample were small. Demirba [25] found a linear correlation between HHV and lignin content. This can explain the increase in HHV of samples after steaming as Lam et al. [11] and others [26] found higher lignin contents for steam treated whitewood samples.

3.6. Carbon content

Table 2 lists data on the elemental analysis of wood species before and after steam treatments. Carbon contents increased from about 46.0% to 57.27% (the highest) for Spruce, and to 52.41%

Table 1
Bulk, tapped and particle solid densities of untreated and treated biomass.

Biomass	Parameter	Bulk density (kg/m^3)		Tapped density (kg/m^3)		Particle density (kg/m^3)		Porosity (decimal)	
		Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Pine	Avg.	151	194	209	243	1387	1117	0.89	0.83
	s.d.	3	6	2	5	6	23	0.00	0.01
Spruce	Avg.	87	129	131	171	1387	1072	0.94	0.88
	s.d.	2	2	4	2	23	13	0.01	0.02
D. Fir	Avg.	175	209	235	273	1407	1177	0.88	0.82
	s.d.	4	8	2	4	21	24	0.01	0.01
Bark	Avg.	310	275	403	338	1400	1455	0.78	0.81
	s.d.	8	7	9	11	0	58	0.01	0.01

$n = 3$.
s.d. Standard deviation.

Table 2
Ultimate and high heat value (HHV) analysis of untreated and steam treated ground biomass.

Biomass	Steam	Parameter	Ash (%)	HHV (MJ/kg)	C (%)	H (%)	N (%)	S (%)	O (%)
Pine	Untreated	Avg.	0.071	18.80	46.65	6.73	0.15	1.04	45.42
		s.d.	0.100	0.10	0.21	0.05	0.01	0.02	0.35
	Treated	Avg.	0.340	21.66	52.81	6.18	0.11	0.92	39.97
		s.d.	0.127	0.23	0.13	0.05	0.01	0.01	0.20
Spruce	Untreated	Avg.	0.215	18.72	46.46	6.46	0.13	0.96	45.99
		s.d.	0.168	0.02	0.13	0.01	0.01	0.00	0.11
	Treated	Avg.	0.938	23.58	57.27	5.78	0.12	0.85	35.97
		s.d.	0.040	0.19	0.01	0.03	0.00	0.01	0.03
D. Fir	Untreated	Avg.	0.144	18.61	46.34	6.56	0.10	0.97	46.02
		s.d.	0.102	0.16	0.00	0.03	0.02	0.01	0.01
	Treated	Avg.	0.279	21.16	52.41	5.94	0.08	0.91	40.65
		s.d.	0.066	0.42	0.04	0.00	0.01	0.01	0.02
Bark	Untreated	Avg.	2.114	19.13	46.98	6.25	0.50	0.90	45.63
		s.d.	0.153	0.31	0.11	0.03	0.01	0.01	0.28
	Treated	Avg.	4.128	22.48	54.52	5.80	0.48	0.87	38.32
		s.d.	2.222	0.16	0.07	0.02	0.01	0.00	0.10

$n = 3$.
s.d. Standard deviation.

Table 3
Color changes after steam treatment.

Species	Parameter		Untreated	Treated	ΔE (s.d.)
Pine	L	Avg.	71.1	31.3	40.4 (0.02)
		s.d.	0.0	0.0	
	a	Avg.	2.3	9.4	
		s.d.	0.0	0.0	
	b	Avg.	17.1	17.4	
		s.d.	0.0	0.0	
Spruce	L	Avg.	71.6	26.4	47.4 (0.06)
		s.d.	0.0	0.0	
	a	Avg.	6.7	5.9	
		s.d.	0.0	0.0	
	b	Avg.	24.7	10.2	
		s.d.	0.0	0.0	
D. Fir	L	Avg.	72.8	28.8	45.3 (0.07)
		s.d.	0.0	0.1	
	a	Avg.	9.0	8.3	
		s.d.	0.0	0.1	
	b	Avg.	25.4	14.5	
		s.d.	0.0	0.1	
Bark	L	Avg.	47.8	20.9	36.4 (0.03)
		s.d.	0.0	0.0	
	a	Avg.	15.4	3.7	
		s.d.	0.0	0.0	
	b	Avg.	26.9	5.4	
		s.d.	0.0	0.0	

$n = 3$.
s.d. Standard deviation.

Table 4
Matrix of correlation coefficient among percent differences between untreated and treated biomass properties.

	ΔL	ΔE	ΔHHV	ΔC
ΔL	1.00	0.92	0.64	0.69
ΔE	0.92	1.00	0.44	0.47
ΔHHV	0.64	0.44	1.00	0.99
ΔC	0.69	0.47	0.99	1.00

ΔL: difference in whiteness.
ΔE: overall color difference.
ΔHHV: difference in calorific value.
ΔC: difference in carbon content.

(the lowest) for D. Fir. Hydrogen and oxygen contents of treated biomass decreased. The amorphous structure of hemicellulose favors the –OH groups to be more reactive to steam. When exposed to steam, the hemicellulose polymer is hydrolyzed. This reaction removes the –OH groups thus lowing the oxygen and hydrogen content and increasing the carbon fraction. Yan et al. [10] showed the carbon content of biomass treated with hot water increased from 50.3% to 56.1% for Pine particles. This increase was associated with considerable decrease in other elemental components such as oxygen, hydrogen, nitrogen and sulfur as is evident in Table 2. The color of carbon is naturally dark gray to black, except when in the hard and crystalline form of diamond. The darker color of treated samples (Fig. 2) could also be an indicator of carbonization during steaming.

Table 4 lists correlation coefficients among untreated and treated biomass properties. Lightness (or whiteness) of untreated and treated biomass species had a correlation of 0.64 and 0.69 with increase in calorific value ΔHHV and Carbon content (ΔC). This is an

Table 5
Equilibrium moisture content (M_e) and moisture adsorption constant (k) before and after treatment.

Biomass	Parameter	Moisture content (%) (d.b.)		Equilibrium moisture content (%) (d.b.)		Adsorption constant (min^{-1})	
		Untreated	Treated	Untreated	Treated	Untreated	Treated
Pine	Avg.	11.2	48.8	11.6	6.7	0.026	0.008
	s.d.	0.1	3.1	0.1	0.3	0.002	0.004
Spruce	Avg.	11.0	41.8	10.3	4.5	0.027	0.006
	s.d.	0.0	3.3	0.1	0.1	0.003	0.005
D. Fir	Avg.	11.1	47.0	9.8	6.6	0.025	0.008
	s.d.	0.0	2.2	0.3	0.1	0.003	0.001
Bark	Avg.	11.1	52.4	13.9	6.9	0.025	0.006
	s.d.	0.2	4.6	0.2	0.2	0.005	0.003

$n = 3$.
s.d. Standard deviation.

Table 6
Comparing steam torrefaction with dry torrefactions on Pine and Spruce particles.

Sample	Species	Temp. (°C)	Residence time (min)	C (%)	HHV (MJ/kg)	Source
Steam treatment	Pine	Untreated	–	46.65	18.80	Present work
		220	5	52.81	21.66	
	Spruce	Untreated	–	46.46	18.72	
		220	5	57.27	23.58	
Dry torrefaction	Pine	Untreated	–	47.21	18.46	[4]
		225	30	49.47	19.48	
		250	30	51.46	20.08	
		275	30	54.91	21.82	
		300	30	63.67	25.38	
Dry fluidized torrefaction	Spruce	Untreated	–	–	18.93	[5]
		280	15	–	20.82	
		290	15	–	21.80	
		300	15	–	22.35	

indication that color may be one of the indicators of carbonization. Further research is needed to steam treat a specific species of biomass to various severities and to develop a statistical significance for correlating color and calorific value.

3.7. Moisture adsorption

Both treated and untreated samples were completely dried in the convection oven at 105 °C for 24 h prior to adsorption test [14]. Table 5 lists equilibrium moisture contents of untreated and treated samples after 180 min of exposure to 30 °C and 90% (RH) in the humidity chamber. The equilibrium moisture content of untreated bark approached an average value of 0.139 (decimal, dry basis), followed by untreated Pine to an average value of 0.116. Untreated Spruce and D. Fir reached an equilibrium moisture content of 0.103. The equilibrium moisture of the treated samples decreased to 0.045 for Spruce and to 0.068 for Pine and bark. As discussed it in previous section, the lowered number of –OH functional groups decreased affinity of treated biomass to moisture. Reduced water adsorption is also the main reason for a decrease in equilibrium moisture content of the treated material. This decrease implies that the treated wood becomes hydrophobic. Moisture adsorption rate (constant k in Eq. (4)) ranged from 0.021 min^{-1} to 0.029 min^{-1} for untreated samples. The adsorption rate decreased slightly to values ranging from 0.019 min^{-1} to 0.028 min^{-1} for the treated wood. Similar trend was also reported by Lam et al. for D. Fir [11]. In our experiments, the decrease in the adsorption rate was the highest for Spruce.

The higher calorific values, higher hydrophobicity and also darker brownish color of steam treated material might be an indicator of a mild torrefaction (carbonization) during steam treatment. Although steam temperature at 220 °C was lower than temperature for dry torrefaction (250–300 °C), steam hastens the heating of the biomass [27]. Table 6 compares the carbon content and higher heating value of untreated and treated Pine particles from this study with those obtained from [4] for Pine and the heat values of this study for Spruce with those published by Li et al. [5]. They did not report carbon contents [5]. Phanphanich and Mani [4] and Li et al. [5] treated biomass samples using hot nitrogen at elevated temperatures of up to 300 °C for duration of 15 and 30 min. The carbon content and HHV of biomass prior to treatments were similar. The carbon content of the yellow Pine subjected to hot nitrogen at 250 °C for 30 min reached 51.4% whereas the treated sample at 220 °C with saturated steam for 5 min had a carbon content of 52.81%. The high calorific value of steam treated sample was similar to the torrefied sample at 275 °C (21.66 vs. 21.82 MJ/kg). For Spruce treated by Li et al. for 15 min, the higher heating values at 300 °C reached to 22.35 MJ/kg [4–5]. The HHV and carbon content of treated wood showed that wet torrefaction could happen at lower temperatures and/or shorter residence time using saturated steam. The comparison between energy consumption of wet vs. dry torrefaction and quality of pellets made of these processes will be included in future work.

4. Conclusions

In this study, debarked Pine, Spruce, and D. Fir whitewood and D. Fir bark were treated with saturated steam at 220 °C for 5 min. The physical and compositional characteristics of treated and untreated biomass were measured and compared. The following conclusions are drawn,

1. Steam treatment increases the calorific value of biomass. The highest increase of 26% in calorific value is observed for Spruce.
2. The carbon content of all treated samples increases. This increase in carbon is comparable to that of dry torrefaction using hot nitrogen.

3. Steam treatment reduces the geometrical mean diameter of particles. This decrease in size is as high as 25%. Bark particles do not show the same degree of size reduction as the debarked fractions do.
4. Loose and tapped bulk density of steam treated bark decreases when compared to untreated biomass. But steam treatment results in an increase in the bulk density of whitewood. Among three species tested, Spruce shows the largest increase in bulk density at 48%.
5. Steam treatment affects the color of particles. On a scale of 0–100 for the "dark to white", the color scale L decreases from an initial value of about 70 (untreated) to around 30, less than half of the initial value after steam treatment. The degree in whiteness has a positive correlation with increased in carbon content.
6. Equilibrium moisture content of steam tread wood decreases when exposed to humid environment. The decrease in the adsorption rate of Spruce is the highest among four samples tested.

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